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**PERCHLORATE
RESEARCH AGENDA
AND
ACTION PLAN**

UNIVERSITY OF CALIFORNIA, RIVERSIDE

Center for Technology Development

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PERCHLORATE RESEARCH AND ACTION PLAN UNIVERSITY OF CALIFORNIA, RIVERSIDE

Background – Perchlorate is a soluble anion used as the primary ingredient of solid rocket propellant as well as for explosives, fireworks, and road flares. First manufactured extensively in the 1940s, it was not until the 1980s that perchlorate was discovered in the environment in California and Nevada. Since 1997, with development of a new ion chromatography analytical method that detects perchlorate at 4 parts per billion (ppb) or below, contamination of ground or surface water has been confirmed in at least 20 states.

Impact – With 16 known sources of perchlorate releases to the environment, California is particularly hard hit. To date, perchlorate has been detected in 319 wells throughout the state. Of these, 78 are in San Bernardino County, 52 in Riverside County, and 25 in Orange County. Further, two release sites in Nevada have resulted in perchlorate contamination of the Colorado River, which provides drinking and irrigation water serving more than 20 million people in California, Arizona, and Nevada.

In April 2003, perchlorate was reported in lettuce grown in the Imperial Valley and irrigated by Colorado River water. This, combined with findings in public water supplies in California ranging from 12 to 811 ppb, has caused concern among policy makers, regulators, and the public. Human health effects are still under study, but perchlorate is known to block the transport of iodine, which is needed for production of the thyroid hormone.

Research Needs – Much is still unknown about perchlorate and its impact on health and the environment. Research is needed on several fronts to develop a comprehensive picture of its effects and measures that can be taken to reduce them. Specific research needs include:

- Assessment of exposure through food and drinking water
- Development of risk management strategies
- Modeling of the fate and transport of perchlorate in the environment
- Study of impacts on terrestrial and aquatic ecosystems, as well as crop systems
- Analysis of perchlorate uptake in agricultural crops
- Development of management practices to minimize accumulation in crops
- Development and field testing of bioremediation systems
- Evaluation of economic impacts

UCR Expertise – The University of California, Riverside (UCR), is uniquely situated to respond to these needs. UCR scientists have extensive experience and expertise in the areas of environmental toxicology, risk assessment, soil chemistry and physics, hydrology, plant physiology, plant molecular biology and plant genetics, microbiology, bioremediation, and environmental resource economics. They have come together under the auspices of UCR's Center for Technology Development to develop a research agenda and action plan for dealing with perchlorate. With UCR's proximity to the Imperial Valley and heavily impacted areas in the Inland Empire, the Center can respond quickly and effectively to the challenges of perchlorate contamination.

Exposure Assessment and Risk Management

The actual risk of perchlorate exposure at environmental levels to human health is not well understood. At what level of exposure does perchlorate cause harm? Over what period of time? Do effects differ by age, gender, or other variables? How long does perchlorate persist in the body? Studies are needed on dietary exposure for various populations—by gender, age, ethnicity, geographic location, and other relevant factors. Such studies must take into account perchlorate consumption through both food and drinking water. To be effective, viable data are needed on food residues, which are currently under development at University of Arizona and Texas Tech. In addition, health end points must be established by No Observed Adverse Effects Levels (NOAELs) and Lowest Observed Adverse Effect Level (LOAELs).

To date, such standards have not been set. The California Office of Environmental Health Hazard Assessment (Cal-OEHHA) has proposed a Public Health Goal (PHG) for water within the range of 2 to 6 parts per billion (ppb); the state has established 4 ppb as an action level for drinking water. No federal standards have been set, but the Environmental Protection Agency has developed interim guidelines with provisional clean-up levels or action levels ranging from 4-18 ppb.

Only after standards are set and dietary exposure is well understood can scientifically based risk management strategies be developed. Further, analytical methods must be reliable down to the lowest end of the allowable spectrum. Once dietary exposure, risk, and risk management strategies are known, this information must be communicated to decision makers and to the public. Outreach efforts will be particularly important in both combating misconceptions and alerting the people to any real dangers and how to minimize or avoid them.

Modeling Fate and Transport

Perchlorate is mobile and highly persistent in the natural environment. As a persistent anion, perchlorate can be modeled with standard approaches, using existing codes. Modeling can be used as an adjunct to proposed treatment technologies, with reaction algorithms that represent the chemical or biological action of a particular treatment method. Modeling can also be used to provide the exposure aspect of an environmental risk assessment under various environmental scenarios.

Some pressing issues can potentially be addressed by modeling or experimentation. Existing perchlorate plumes can be evaluated in terms of residence time and ultimate destination, based on different treatment options. In some areas, blending of perchlorate contaminated water with non-contaminated water has been proposed; modeling can be used to determine to what extent this will lower concentrations, and over what timeframe. It can also help discover whether natural attenuation through the soil before ultimately mixing with groundwater will reduce perchlorate contamination below harmful levels.

In addition, modeling can be useful in terms of agricultural impacts, by answering such questions as: What are the best irrigation and crop management strategies to minimize perchlorate uptake and accumulation in food crops? Is there a closed perchlorate cycle from soil or irrigation water

to forage crops to animals and then through animal waste back to soil? How do soil types, irrigation management, and various crops affect perchlorate entering the food chain? The answers to these questions can help in development of Best Management Practices.

Finally, an important use of modeling is in evaluation of potential treatments, including likely effectiveness of proposed treatment strategies (such as whether perchlorate can be immobilized or neutralized in the soil or groundwater), determination of clean-up costs, and cost-benefit analyses.

Ecosystem Impacts

At present, virtually nothing is known regarding potential impacts of perchlorate on key organisms in contaminated ecosystems. The extent to which perchlorate bioaccumulates in food webs has not been determined. Studies are needed on population level impacts of this pollutant with organisms at the bottom of the food chain. Changes in species occurrence and population densities of these organisms have profound effects on ecosystem health and function in both natural and agricultural systems. For example, little is known about arthropod behavioral, reproductive, and longevity responses to perchlorate for herbivores, detritivores (scavengers), and medically important pests such as mosquitoes. Additional research is needed on quantifying occurrence (or lack of occurrence) of biotransfer/biomagnification of perchlorate to predators, and on interactive effects of perchlorate with other common pollutants such as selenium, MBTE, and chromium VI.

Also unknown is how perchlorate partitions among different environmental compartments when it enters an ecosystem. Modeling is one method of conducting such an evaluation. It can then be determined whether perchlorate is causing unwanted effects on ecosystems or ecosystem components, such as toxicity to specific organisms or impacts on aquatic or terrestrial ecosystems. In conducting such studies, the accuracy of analytical detection methods is critical.

It is likely that perchlorate may behave conservatively, as does chloride. If this is the case, agricultural drainage water would have perchlorate concentrations substantially higher than the irrigation water, which would be determined by the irrigation management and leaching fraction. In the Imperial Valley, where the soils are fine textured and leaching fractions are low, drainage water concentrations could be up to 10 times the irrigation water concentrations. Drainage ditches, evaporation ponds, and the Salton Sea could have substantially higher concentrations of perchlorate, and ecotoxicological hazards may be seen in these environments.

Agricultural drainage water is often reused for wetland habitat, and to remove nutrients and suspended solids from the water. Redox-sensitive elements, such as selenium and uranium, accumulate in the sediments of wetlands due to the anaerobic conditions found below the sediment/water interface. The products of perchlorate reduction are non-toxic, suggesting that wetland treatment may be a viable method for dealing with contaminated drainage water. However, plant uptake of perchlorate under wetland conditions need to be studied. Another aspect of such an investigation is whether and to what extent perchlorate is broken down by existing plant and other aquatic organisms.

Plant Uptake

Of immediate concern to growers irrigating their crops with Colorado River or other contaminated water is the potential uptake of perchlorate by crops, including vegetables and hay. Such accumulation may have significant economic implications for both the agricultural industry and consumers. Existing data are scattered and inconclusive, and the analytical method used in reported findings has not been carefully scrutinized. A precise evaluation of the problem is needed. The first step requires development of methods for accurate analysis of perchlorate in plant tissues, plant and soil extracts, milk, urine, and saline waters such as agricultural drainage water.

Once this is accomplished, the next step is to evaluate the mechanisms and pathways for perchlorate transfer and partition from soil/irrigation water to plant tissues. Factors to be investigated include genotypic differences in uptake and partitioning of perchlorate, both across important crop species and across cultivars of certain important crops (e.g., lettuce). In addition, systematic investigation is needed on the influences of salinity and competing ions on perchlorate uptake, as these factors may be significant and can, to some degree, be managed in production fields. For this, it is important to understand the fate of perchlorate in soils, as it may affect the availability for plant uptake. Laboratory experiments are needed to understand the effects of soil conditions on transformation of perchlorate, to determine adsorption of perchlorate on soil minerals and soil organic matter, and to identify the rates of perchlorate reduction under reducing conditions and limiting factors.

Crop Management

In agricultural systems, plant uptake of perchlorate may be reduced with effective farming practices. A better understanding is needed of the dependence of perchlorate uptake on common management factors such as soil types, crop types, and irrigation practices. Increasing or decreasing the leaching fraction in the field, for example, will change the concentration of perchlorate and the competing ions in the root zone. Therefore, careful study is needed comparing such impacts using sprinklers, surface drip irrigation, subsurface drip irrigation, and furrow irrigation on crops representative of the current crop profile in the affected region. Rigorous statistical analysis will yield data to determine the most effective combination of management techniques.

A tool that may be used in crop management is a Geographical Information System (GIS) to understand changes in perchlorate over large areas. The results can be used to determine the extent of the problem and how environmental and other factors affect perchlorate contamination.

Crop production practices that increase soil organic matter or microbial activity may also affect perchlorate concentrations in food and water. Soils must be analyzed for organic matter content, texture, pH, and composition of major cations and anions. Factors or practices that result in significantly lower perchlorate accumulation by crops can be identified and used to develop one or more sets of low-risk management practices that growers can adopt. In developing these best management practices, economic, social, and other factors will be simultaneously considered so that the practices will be highly feasible for implementation. Field demonstrations, growers'

workshops, and other outreach activities will be needed, involving interested parties such as UC researchers, county farm advisors, water districts, growers' associations, commodity boards, and water quality regulators to facilitate information dissemination and technology transfer.

In the longer term, plant molecular biology and genetics will allow researchers to understand the mechanisms of perchlorate toxicity and to identify genes required by plants for resistance and/or tolerance to toxic soil components. This in turn may lead to the development of genetically engineered plants that can tolerate perchlorate in their environment without taking it up, or by generating plants that may be used to remediate perchlorate contaminated areas.

Bioremediation

A reliable, cost effective technology is needed to remove perchlorate from contaminated wells and from irrigation water derived from the Colorado River. Bioremediation is a promising technique for treatment of perchlorate, and has been used successfully in both in-situ and ex-situ treatment approaches. Our new technology involves stimulating microbial respiration in an open channel reactive biobarrier in which bacteria use a lignocellulytic organic substrate providing asource of carbon and energy. Various bacteria couple oxidation of the added substrate with reduction of perchlorate, following depletion of available oxygen. This destroys perchlorate, converting it to chloride and oxygen, which are both harmless to crops and the environment.

Development of this concept requires laboratory studies and a field pilot study. An initial step must be to understand and optimize the microbiology for efficient perchlorate reduction under conditions relevant to the treatment system. This requires identification of several sources of electron donor/bacterial support materials that may be available locally, isolating substrate-specific bacterial or fungal cultures, and studying them in perchlorate-impacted water in order to elucidate relevant mechanisms and parameters. After characterizing the isolates through molecular fingerprinting, this work should result in selection of one or two suitable substrates and associated microbial monocultures that can bring about efficient perchlorate reduction.

Construction of a laboratory-scale treatment system will enable researchers to conduct studies to obtain a preliminary evaluation of relevant engineering parameters under simulated field conditions. The final step is to conduct a field-scale pilot test to verify laboratory results, adjust as necessary, and develop a detailed cost estimate for full scale applications. If successful, users could treat large volumes of irrigation water, drainage water, groundwater, surface water, and/or waste streams contaminated with perchlorate. The proposed system is potentially far more economical than existing technolgies and requires little or no input and maintenance. Effluent meeting regulatory standards could safely be used for irrigation, discharged to surface water bodies, or used to recharge groundwater resources.

Economic Impacts

Significant costs are associated with perchlorate contamination—costs associated with monitoring, evaluation, and clean-up. Of significant interest are economic impacts associated with groundwater availability and use. Southern California's groundwater storage is an increasingly important resource that allows water districts to meet demand in dry years.

Perchlorate contamination could pollute some aquifers to the point where they could no longer be used for groundwater storage. Water agencies would then be forced to choose between more expensive storage options or rationing water for dry years. The costs of recovering the groundwater storage resource through remediation are also very high. Research could determine whether the groundwater storage capability is worth the cost of remediation.

The effects on agricultural profitability and production could also be significant, particularly if perchlorate standards are implemented. Losses may occur to growers if consumers refrain from buying produce they fear is contaminated; growers will also bear the cost of implementing new irrigation practices or other management strategies to reduce perchlorate uptake. Less tangible costs are associated with human health—important information for regulatory decision-making—and the long-term impact on ecosystems. Research is needed to examine these economic impacts and to contrast the expense associated with mitigation or clean-up strategies with that of not doing anything.

UCR Expertise

The University of California, Riverside, has expertise in each of the areas identified above. With its long tradition of agricultural research and outreach, UCR is well equipped to respond to the needs of the agricultural industry on issues relating to perchlorate uptake by crops; best management practices, including irrigation; and, in the longer term, development of resistant crops. A major part of UCR's agricultural mission is environmental and natural resource management. The campus offers great depth of expertise for dealing issues related to risk assessment, fate and transport of perchlorate through soil and water, ecosystem impacts, and bioremediation. For field-testing and outreach purposes, UCR can take advantage of the state's extensive Cooperative Extension network. Further, the proximity of UCR to both Imperial Valley agriculture and a high concentration of perchlorate-contaminated wells allows the campus to utilize these areas for extensive field testing while, at the same time, being responsive to critical needs. UCR faculty have come together under the auspices of the Center for Technology Development, directed by Dr. William Frankenberger, to develop research and outreach programs related to perchlorate. Experts are listed below:

Christopher Amrhein
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Area of specialization: Soil and water chemistry of inorganic contaminants; redox processes. Perchlorate analysis, plant uptake, and partitioning mechanisms.

W. Bowman Cutter
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Area of specialization: Public economics, environmental economics, and applied econometrics.

William T. Frankenberger
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Area of specialization: Bioremediation of perchlorate, selenium and arsenic in soil and water; development of methods for perchlorate analysis.

Jay J. Gan
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Area of specialization: Fate, transport, and mitigation of toxic elements in the environment; water pollution and prevention. Perchlorate analysis and field management practices to reduce crop uptake.

William Jury
Distinguished Professor of Soil Physics
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Area of specialization: Measurement and modeling of organic and inorganic chemical movement and reactions in field soils; development and testing of organic chemical screening models; characterization of the spatial variability of soil physical and chemical properties; and evaluating volatilization losses of organic compounds. Modeling the fate and transport of perchlorate.

Bob Krieger
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Area of specialization: Development and the use of advanced analytical methodology to identify movement of perchlorate from environmental compartments to children and adults. The exposure assessment process, development of risk management and, particularly, risk perception data, as part of risk communication.

Paul B. Larsen
Assistant Professor
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Area of specialization: Plant molecular biology and plant molecular genetics. Identification of genes required by plants for resistance and/or tolerance to toxic soil components, and engineering plants that can grow in these environments.

Milt McGiffen

Associate CE Vegetable Crops Specialist and Assistant Plant Physiologist

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Area of specialization: Models of cropping systems and population dynamics. Effects of agriculture on the environment, including the effect of farming practices on perchlorate concentrations in food and water.

David R. Parker

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Area of specialization: Soil chemistry and plant nutrition; chemistry and bioavailability of trace elements. Perchlorate analysis and plant uptake and partitioning mechanisms.

John Trumble, Ph.D.

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Area of specialization: Plant compensation for insect herbivory; biological and microbial control in sustainable agriculture; impact of air and heavy metal pollution on plant/insect interactions.

Laosheng Wu

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Area of specialization: Measurement and modeling water and solute transport in field soils; development of best management practices to maximize water and fertilizer use efficiency and minimize surface and ground water pollution; research on irrigation uniformity effect on crop yield and nitrate leaching, infiltration measurement and modeling, shallow groundwater management, and instrumentation and methodology for measuring soil physical properties.